Removal of Toxic Gases on Strong/and Weak-Base Anion Exchange Fibers

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Abstract: In this study, a strong-base ion exchange fiber, APP-g-GMA, was synthesized by grafting GMA onto a PP trunk polymer, using an E-beam accelerator for the purpose of pre-irradiation, in order to remove sulfur dioxide and nitrogen dioxide. A weak-base ion exchange fiber, AN-co-MMA, was spun by wet-spinning and was functionalized by hydrolysis. To determine the effects of various conditions, such as the SO₂ and NO₂ concentrations and the water content in the column, we investigated the adsorption for SO₂ and NO₂ over two types of fibrous ion-exchangers. The adsorption rate constants were calculated from macroscopic models by a linear square fitting method. SO₂ and NO₂ removal on the fibrous ion-exchangers both depend on the initial concentration of SO₂ and NO₂. The removal efficiency of NO₂ and SO₂ on the weak-base anion exchange fiber was slightly affected by initial water contents of > 10 g. Also, the removal efficiency of NO₂ on the strong-base ion exchange fiber was slightly dependent on the initial water content at a water content of > 20 g.

Keywords: fibrous ion exchanger, sulfur dioxide, nitrogen dioxide, gas removal

Introduction

Sulfur dioxide (SO₂) and nitrogen oxides (NOₓ) caused by excessive energy consumption are major sources of air pollution. However, with regard to NOₓ removal, it is more important to control NOₓ than NO because NO is converted into the more harmful NO₂ in the atmosphere [1]. Currently, there are many different processes that are used for the removal of SO₂ and NOₓ [2]. In terms of SO₂ removal, wet desulfurization using limestone is widely employed because of its low cost, although the use of the dry desulfurization process, using lime or limestone, is also fairly widespread. In terms of NOₓ removal, SCR (selective catalytic reduction) processes are commonly used, but they have faults, such as exhausting unreacted ammonia and decreasing NOₓ removal efficiency through side reactions. Another method of NOₓ removal is to use adsorbents. The commonly used adsorbents are carbon, activated carbon fiber, zeolite, activated carbon, and silica gel. Lee and coworkers [3] examined the adsorption of NOₓ and SO₂ on activated carbon impregnated with KOH. Despres and coworkers [4] prepared Cu-ZSM-5 with Na-ZSM-5 and studied the mechanism of adsorption and the influence of water on the adsorption of NO₂. Kopac and coworkers [5] investigated the adsorption equilibrium and adsorption rate of sulfur dioxide on silica gel. They found that the Freundlich model gave the best fit, suggesting the existence of a surface adsorption mechanism, and they investigated the effects of the initial SO₂ concentration and temperature. Shirahama and coworkers [6] studied the adsorption and reduction of NO₂ over pitch-based ACFs at different concentrations and temperatures. Mochida and coworkers [7,8] investigated the kinetics of the continuous removal of SO₂ on PAN-based activated carbon fibers. In addition, ion-exchange fibers (IEFs) that have a high selectivity can be good adsorbents for SO₂ and NO₂ removal [9], although most ion-exchange fibers have been used to adsorb some ions during water purification [10,11]. Moreover, if using IEFs instead of the SCR process, NOₓ removal can be performed after modifying the existing SCR process slightly. In this study, two types of ion exchange fibers were synthesized by copolymerization and E-beam pre-

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Table 1. Basic Properties of the Two Types of Fibrous Ion Exchanger (IEF)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Strong base IEF</th>
<th>Weak base IEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functionalization</td>
<td>Amination</td>
<td>Hydrolysis</td>
</tr>
<tr>
<td>Trunk polymer</td>
<td>PP fiber</td>
<td>PAN copolymer</td>
</tr>
<tr>
<td>Functional group</td>
<td>-N(CH₃)₂Cl</td>
<td>-NH₂, -NH</td>
</tr>
<tr>
<td>Ion exchange capacity (meq/g)</td>
<td>1.7</td>
<td>4.5</td>
</tr>
<tr>
<td>Water uptake (g H₂O/g)</td>
<td>1.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>

irradiation, respectively. SO₂ and NO₂ were removed from a gas stream by using these strong/and weak-base ion exchange fibers under conditions of varying water content, gas concentration, and gas flow rate.

**Experimental**

**Materials**

PP-g-GMA was synthesized by GMA grafting onto a PP trunk polymer using an E-beam accelerator for pre-irradiation. A strong-base fibrous ion exchanger, APP-g-GMA of -Cl type containing trimethylammonium, was prepared by amination [10]. PP-g-GMA was placed in DMSO/H₂O solution at 40°C for 2 h and, after adding NaI, TMA, and TEA, the reaction mixture was left for 12 h before being washed in 0.1 N HCl and deionized water, and then it was dried at 55°C for 24 h. A PAN copolymer was synthesized using acrylonitrile (AN) and methyl methacrylate (MMA) and was spun by wet-spinning. A weak-base fibrous ion exchanger, PAN ion exchanger containing -NH₂ and -NH, was prepared by hydrolysis [11]. PAN copolymer and H₂SO₄ were agitated at 50°C for 3 h, washed in deionized water, and dried at 50°C. The characteristics of the fibrous ion exchangers are given in Table 1.

The sulfur dioxide and nitrogen dioxide gases were purchased from Korea Standard Gas Co., Korea. The gases (assay 99.9%, 50000 ppm) used for the simulation were diluted. Acrylonitrile and methyl methacrylate were purchased from Sigma Chemical Co., Ltd. Polypropylene fiber was purchased from Jeon-Bang Industry Co., Korea. Glycidyl methacrylate (assay 98%), polyvinylalcohol, hydrochloric acid, and sulfuric acid were purchased from Junsei Chemical Co., Ltd. Other reagents were of analytical grade or higher.

**Methods**

An acryl column (4.5 cm in width and 6 cm in height) was used to adsorb the sulfur dioxide and nitrogen dioxide; 17 g of IEF was packed in the column with, in each case, the appropriate amount of water. A schematic diagram of the SO₂ and NO₂ adsorption apparatus is shown in Figure 1. The flow rates of the simulated SO₂ and NO₂ gases were controlled by means of an MFC (Mass Flow Controller, Sierra Ins.) and, in this way, the gases were fed into the bottom of the column at different inlet concentrations and flow rates. An SO₂ analyzer (Thermo Environmental Inst., USA) and an NO₂ analyzer (Thermo Environmental Inst., USA) were used to analyze the outlet SO₂ and NO₂ concentrations, respectively. All experimental conditions are given in Table 2.

**Results and Discussion**

**Calculation of Adsorption Rate Constant [12]**

The macroscopic model, which can be used to determine the adsorption rate constant in the column test, is represented by

\[
\ln\left(\frac{C_o - C}{C_o}\right) = k_1 C_o t - \frac{R_q M}{F} = k_1 C_o \left(1 - \frac{q_c M}{C_o F}\right) \tag{1}
\]

where C (ppm) represents the outlet SO₂ and NO₂ concentrations, C₀ (ppm) represents the inlet SO₂ and NO₂ concentrations, k₁ is the rate constant [1/(ppm·h)], qc is the equilibrium concentration of the sorbed solute (ppm/g), M is the mass of the fiber (g), F is the flow rate (L/min), and t is the time (min). To solve the equation...
Table 2. Experimental Conditions used for the SO₂ and NO₂ Adsorption Tests

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂ concentration (ppm)</td>
<td>340 ~ 1200</td>
</tr>
<tr>
<td>NO₂ concentration (ppm)</td>
<td>50 ~ 300</td>
</tr>
<tr>
<td>Gas flow rate (L/min)</td>
<td>20 ~ 40</td>
</tr>
<tr>
<td>O₂ concentration (%)</td>
<td>3</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
</tr>
<tr>
<td>Water content (gH₂O)</td>
<td>5 ~ 30</td>
</tr>
</tbody>
</table>

with the linear-squares fitting method, this equation can be rewritten as

\[ \ln \left( \frac{C_0 - C}{C} \right) = k(t-\tau) \]

(2)

where \( k = k_1 C_0 \), and \( \tau = \frac{qM}{C_0 F} \).

Using linear fitting of \( \ln \left( \frac{C_0 - C}{C} \right) \) vs \( t \) with the least-squares fitting method, all parameters were obtained and are listed in Table 3.

As shown in Table 3, the adsorption rate constant decreased with increasing gas concentration and increasing water content, in the case of SO₂ removal on the IEFs. Also, in the NO₂ removal process, the adsorption rate constant decreased with increasing inlet gas concentration. Under the same conditions, in the cases of both SO₂ and NO₂ removal, the strong-base IEFs exhibited higher values of adsorption rate constant.

Adsorption Properties of Sulfur Dioxide on IEFs

Effect of Inlet SO₂ Concentration

Figure 2 shows the breakthrough curves for the removal of SO₂ on the strong and weak-base ion exchange fibers at a constant water content and gas flow rate. Figure 3 illustrates the breakthrough profiles on the weak-base ion exchange fiber at various inlet concentrations.

Generally, the selectivity and adsorption rates of strong-base ion exchangers are higher than those of weak-base ion exchangers [13]. In this study, however, as shown in

![Figure 2. Outlet SO₂ concentration as a function of reaction time for the two types of IEFs at 25°C (inlet SO₂: 340 ppm; flow rate: 30 L/min; water content: 10 g; O₂ concentration: 3%).](image)

![Figure 3. Outlet SO₂ concentration as a function of reaction time for various concentrations at 25°C (flow rate: 30 L/min; water content: 10 g; O₂ concentration: 3%).](image)

Figure 2, the breakthrough time for SO₂ removal on the

Table 3. Results of Linear Fitting and Adsorption Rate Constant on IEFs

<table>
<thead>
<tr>
<th>Ion exchange fiber</th>
<th>Gas</th>
<th>Conc. (ppm)</th>
<th>Flow rate (L/min)</th>
<th>Water content (g)</th>
<th>Equations</th>
<th>( K_1 ) [ppm min⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong-base IEF</td>
<td>SO₂</td>
<td>340</td>
<td>30</td>
<td>10</td>
<td>( y = 0.177x - 6.8208 )</td>
<td>0.000521</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>30</td>
<td>10</td>
<td>( y = 0.167x - 5.5255 )</td>
<td>0.000278</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1200</td>
<td>30</td>
<td>10</td>
<td>( y = 0.220x - 6.4117 )</td>
<td>0.000183</td>
</tr>
<tr>
<td>Weak-base IEF</td>
<td>SO₂</td>
<td>340</td>
<td>30</td>
<td>10</td>
<td>( y = 0.290x - 2.0432 )</td>
<td>0.000853</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>30</td>
<td>20</td>
<td>( y = 0.017x - 2.9363 )</td>
<td>0.000050</td>
</tr>
<tr>
<td>Strong-base IEF</td>
<td>NO₂</td>
<td>100</td>
<td>20</td>
<td>20</td>
<td>( y = 0.028x + 0.8190 )</td>
<td>0.000275</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>20</td>
<td>20</td>
<td>( y = 0.017x + 0.4721 )</td>
<td>0.000080</td>
</tr>
<tr>
<td>Weak-base IEF</td>
<td>NO₂</td>
<td>100</td>
<td>20</td>
<td>20</td>
<td>( y = 0.013x + 0.8190 )</td>
<td>0.000130</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>20</td>
<td>20</td>
<td>( y = 0.018x + 0.0919 )</td>
<td>0.000086</td>
</tr>
</tbody>
</table>
strong-base IEF is shorter than that on the weak-base IEF, although the strong-base IEF has a higher selectivity and reactivity. Because the two types of IEFs were synthesized using different methods, and the functionalization of the weak-base IEF with hydrolysis went well, the weak-base IEF had a high ion exchange capacity. Therefore, the breakthrough time on the weak-base IEF is longer than that on the strong-base IEF in the case of SO$_2$ adsorption. In Figure 3, we observe that the breakthrough time, when the outlet concentration of SO$_2$ is equal to zero, decreased with increasing inlet SO$_2$ concentration, with values of 28 and 18 min at SO$_2$ concentrations of 300 and 900 ppm, respectively. Because SO$_2$ is easily sorbed into water and is subsequently ionized to sulfate and bisulfite at high concentrations, we predict that high inlet concentrations cause the breakthrough time to be reduced.

**Effect of Water Content on IEFs**

Ion exchangers can swell in water and polar solvents, but only to a limited degree. Also, the higher the swelling ratio of the ion exchanger, the higher the ion exchange capacity. Thus, it is important to control the amount of water used in the column test. In the column test, both sulfur dioxide and nitrogen dioxide were easily absorbed into water when a large amount of water was present.

Figure 4 indicates that SO$_2$ was completely removed from the strong-base IEF and the weak-base IEF after 8 and 28 min, respectively. Also, Figure 4 illustrates that the breakthrough time was changed slightly at an initial water content of >10 g on the weak-base IEF and was changed slightly at an initial water content of >20 g on the strong-base IEF. Thus, we found that minimum water content of the strong-base IEF necessary for SO$_2$ removal was 20 g and that of the weak-base IEF was 10 g.

**Adsorption Properties of Nitrogen Dioxide on IEFs**

**Effect of Inlet NO$_2$ Concentration**

Figures 5 and 6 show the breakthrough curves for the removal of NO$_2$ on the strong and weak-base ion exchange fibers at constant water content and gas flow rate.

Figures 5 and 6, confirm that the removal efficiency of NO$_2$ on the ion exchange fiber is lower than that of SO$_2$ on the IEF, because of the lower solubility of NO$_2$. Also, we observe that the slope of the breakthrough curve and the removal efficiency increased upon increasing the gas concentrations, because the absorption and ionization of NO$_2$ functioned well and the ion exchange rate between ionized NO$_2$ and the functional groups of the ion exchange
fiber increases at high NO$_2$ concentrations. It can be predicted that the strong-base IEF has a good selectivity for NO$_2$, although the strong-base IEF has a lower ion exchange capacity than the weak-base IEF.

**Effect of Water Content on IEFs**

In the NO$_2$ adsorption test, the absorption of NO$_2$ into water depended on the water content of the fibrous ion exchangers. Thus, the NO$_2$ adsorption experiment was performed using 200 ppm NO$_2$ at a flow rate of 20 L/min for various initial water content.

Figure 7 shows the influence of water content on adsorption over the weak-base IEF. In Figure 7, we see that the breakthrough profiles were similar at water contents of > 10 g. Thus, in the results shown in Figures 4 and 7, we see that the removal efficiency of both NO$_2$ and SO$_2$ on the weak-base anion exchange fiber is affected slightly by the initial water content at a water content of > 10 g.

Figure 8 illustrates the effect of water content on the adsorption over the strong-base anion exchange fiber. As shown in Figure 8, the removal efficiency of NO$_2$ on the strong-base IEF depended slightly on the water content, at water contents of > 20 g. In comparing the SO$_2$ adsorption on the IEFs, NO$_2$ was not completely removed from the ion exchange fibers. However, it can be predicted that the ion exchange fibers have a good affinity for these gases and can be used in the air purification process, without catalysts, because of their low cost and simplicity. Also, although the strong anion exchange fiber had a low ion exchange capacity, the removal efficiencies of NO$_2$ on the two types of ion exchange fiber were similar, so that it can be considered that the strong-base ion exchange fiber has good selectivity for NO$_2$.

**Prediction of Adsorption and Desorption Mechanism of IEFs**

The predicted adsorption and desorption mechanism for SO$_2$ and NO$_2$ removal on the strong-base anion exchange fiber is shown in Figure 9.

SO$_2$ is easily absorbed into water, which is present in the IEF, and converted into sulfurous acid. Then, the bisulfite ions and sulfite ions react with the chloride of the IEF, with the result that they become more stable. After all of the functional groups of the ion exchange fiber have reacted with sulfurous acid, the ion exchange fiber needs to be regenerated with alkali solutions. Also, NO$_2$ is converted into nitrate, although the absorption rate of NO$_2$ is lower than that of SO$_2$. In this study, to regenerate the IEFs, after the adsorption experiment, 5 wt% NaOH solution was used. As shown in Figure 9, sodium bisulfite, sodium sulfite, and sodium nitrate can exist in the regeneration solution, and the functional groups of the IEF were converted to the CI form after regeneration. Thus, the optimum exchange time with the regeneration solution can be calculated from the results of the ion exchange adsorption test, combined with observations regarding the change in pH. Also, the development of a more-effective ion exchange fiber could be envisaged, by using special functional groups having the ability to control the selectivity for sulfate and nitrate [14].

**Amount of SO$_2$ and NO$_2$ Adsorbed**

Table 4 shows the adsorption quantity of SO$_2$ and NO$_2$ for various experimental conditions at C/Co = 0.8.

For SO$_2$ removal, the adsorption quantity on two types of IEFs was 0.3212 ~ 2.6515 mmol per 1 g fiber under various conditions and that increased with increasing SO$_2$.
Table 4. Concentrations of SO₂ and NO₂ Adsorbed and Experimental Conditions (C/C₀ = 0.8)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Inlet Conc. (ppm)</th>
<th>Flow rate (L/min)</th>
<th>Water content (g)</th>
<th>Weak-base anion exchange fiber</th>
<th>Strong-base anion exchange fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Adsorption quantity (mmol gas/g IEF)</td>
<td>Adsorption quantity (mmol gas/g IEF)</td>
</tr>
<tr>
<td>SO₂</td>
<td>340</td>
<td>30</td>
<td>20</td>
<td>1.0449</td>
<td>0.3212</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>30</td>
<td>10</td>
<td>1.6022</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>30</td>
<td>10</td>
<td>2.6515</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>20</td>
<td>20</td>
<td>0.00549</td>
<td>0.00106</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>20</td>
<td>20</td>
<td>0.02693</td>
<td>0.02279</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>20</td>
<td>5</td>
<td>0.06113</td>
<td>-</td>
</tr>
<tr>
<td>NO₂</td>
<td>200</td>
<td>20</td>
<td>10</td>
<td>0.1206</td>
<td>0.09499</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>20</td>
<td>20</td>
<td>0.19482</td>
<td>0.21912</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>20</td>
<td>30</td>
<td>0.17367</td>
<td>0.23804</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>20</td>
<td>20</td>
<td>0.30427</td>
<td>0.24603</td>
</tr>
</tbody>
</table>

1. Adsorption

\[
\text{SO}_2(g) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3(aq)
\]

\[
\text{H}_2\text{SO}_3(aq) \rightarrow \text{H}^+ + \text{HSO}_3(aq)
\]

\[
\text{HSO}_3(aq) \rightarrow \text{H}^+ + \text{SO}_3^{2-}(aq)
\]

\[
\text{NO}_2(g) \rightarrow \text{NO}_2(l)
\]

\[
\text{NO}_2(l) + \text{OH}^- \rightarrow \text{NO}_3^-
\]

\[
\text{R-} \text{N(CH}_3)_2\text{Cl}^- + \text{HSO}_3^- \rightarrow \text{R-} \text{N(CH}_3)_2\text{HSO}_3^-
\]

\[
\text{R-} \text{N(CH}_3)_2\text{Cl}^- + \text{SO}_3^{2-} \rightarrow (\text{R-} \text{N(CH}_3)_2\text{SO}_3^2-)
\]

\[
\text{R-} \text{N(CH}_3)_2\text{Cl}^- + \text{NO}_3^- \rightarrow \text{R-} \text{N(CH}_3)_2\text{NO}_3^-
\]

2. Desorption

\[
\text{R-} \text{N(CH}_3)_2\text{HSO}_3^- + \text{NaOH} \rightarrow \text{R-} \text{N(CH}_3)_2\text{Cl}^- + \text{NaHSO}_3
\]

\[
(\text{R-} \text{N(CH}_3)_2\text{SO}_3^2- + 2\text{NaOH} \rightarrow 2(\text{R-} \text{N(CH}_3)_2\text{Cl}^-) + \text{Na}_2\text{SO}_3
\]

\[
\text{R-} \text{N(CH}_3)_2\text{NO}_3^- + \text{NaOH} \rightarrow \text{R-} \text{N(CH}_3)_2\text{NO}_3^- + \text{NaNO}_3
\]

**Figure 9.** Prediction of the adsorption and desorption mechanisms on strong-base anion exchange fiber.

Concentration, as we predicted. Under the same experimental conditions, the weak-base anion exchange fiber has three times as much adsorption quantity as does the strong-base anion exchange fiber. For NO₂ removal, the adsorption quantity changed from 0.00106 to 0.303772 mmol/g fiber at different concentrations and water contents on the IEFs. In Table 4, the amount of adsorbed NO₂ increased with increasing inlet NO₂ concentrations from 50 to 300 ppm to values of was 0.00549 to 0.304272 mmol/g fiber. Also, the amount of adsorbed NO₂ at a water content of 10 to 30 g increased three times as much as that at a water content of 5 g.

**Conclusions**

In this study, the sulfur dioxide and nitrogen dioxide gases were removed by means of strong/and weak-base ion exchange fibers, which were functionalized by amidation and hydrolysis, respectively. In the column test, the breakthrough time decreased as the inlet SO₂ and NO₂ concentrations increased. However, the water contents of the weak and strong-base ion exchange fibers slightly affected the breakthrough profiles at initial water contents of >10 g and >20 g, respectively. The adsorption rate constants were calculated by means of macroscopic modeling equations. Following the adsorption test, the removal efficiencies of NO₂ on two types of ion exchange fiber were similar, so that it can be considered that the strong-base ion exchange fiber has a good selectivity for NO₂, although the strong anion exchange fiber has a lower ion exchange capacity than does the strong-base IEF. In the SO₂ adsorption test, the adsorption quantities on the two types of IEFs were 0.3212 to 2.6515 mmol per 1 g fiber under various conditions and these values increased upon increasing the SO₂ concentration. In the NO₂ adsorption test, the adsorption quantities changed from 0.00106 to 0.303772 mmol/g fiber at different concentrations and water contents on the IEFs. Based on these results, we believe that the fibrous ion exchangers, which were synthesized by two different methods, are good adsorbents and can be employed for the removal of SO₂ and NO₂.
Acknowledgment

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References